

# Toward a Comprehensive Model of Snow Crystal Growth:

## 3. The Correspondence Between Ice Growth from Water Vapor and Ice Growth from Liquid Water

Kenneth G. Libbrecht

Department of Physics, California Institute of Technology  
Pasadena, California 91125

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**Abstract.** We examine ice crystal growth from water vapor at temperatures near the melting point, when surface premelting creates a quasiliquid layer at the solid/vapor interface. Recent ice growth measurements as a function of vapor supersaturation have demonstrated a substantial nucleation barrier on the basal surface at these temperatures, from which a molecular step energy can be extracted using classical nucleation theory. Additional ice growth measurements from liquid water as a function of supercooling exhibit a similar nucleation barrier on the basal surface, yielding about the same molecular step energy. These data suggest that ice growth from water vapor and from liquid water are both well described by essentially the same underlying nucleation phenomenon over a substantial temperature range. A physical picture is emerging in which molecular step energies at the solid/liquid, solid/quasiliquid, and solid/vapor interfaces create nucleation barriers that dominate the growth behavior of ice over a broad range of conditions. Since the step energy is an equilibrium quantity, just as surface melting is an equilibrium phenomenon, there exists a considerable opportunity to use many-body simulations of the ice surface structure and energetics at equilibrium to better understand many dynamical aspects of ice crystal growth.

## 1 Introduction

Recent measurements of ice growth rates from water vapor have shown a characteristic nucleation-limited behavior, with the growth velocity normal to the surface exhibiting the exponential dependence  $v_n \sim \exp(-\sigma_0/\sigma)$ , where  $\sigma$  is the water vapor supersaturation relative to ice at the surface and  $\sigma_0$  is a parameter extracted from the data [1]. Classical nucleation theory allowed the authors to calculate the free energy (per unit length) of a molecular step on the crystal surface from the measured  $\sigma_0(T)$ , thus yielding the step energy as a function of temperature for the basal and prism facets. Near the melting point, specifically at  $T = -2$  C, values of  $\sigma_0 \approx 0.4$  percent on the basal surface and  $\sigma_0 < 0.01$  percent on the prism surface were reported. The substantially larger nucleation barrier on the basal surface provides a simple explanation for the formation of thin plate-like crystals at this temperature, an observation first made nearly 75 years ago [2].

It has similarly been long known that growing free-standing ice crystals in liquid water at small undercoolings results in the formation of thin plate-like crystals [3], and quantitative measurements of the basal growth velocity over a half-century ago yielded a similar exponential dependence  $v_n \sim \exp(-\Delta T_0/\Delta T)$ , where  $\Delta T = T_m - T_{surf}$  is the supercooling at the growing interface,  $T_m$  is the melting temperature, and  $\Delta T_0 \approx 0.24$  C is an experimentally determined constant [4]. This functional form is again indicative of a nucleation barrier, and the molecular step energy can be calculated from  $\Delta T_0$ . Similar measurements for the growth of the prism surface yielded a much lower nucleation barrier, again consistent with the formation of

thin plate-like crystals.

It is also well known that surface premelting is an important structural feature of the ice solid/vapor interface [5]. In essence, the molecular layers near the crystalline surface are not as tightly bound as in the bulk, resulting in the formation of an amorphous “quasiliquid” layer (QLL) at the interface. The detailed properties of the quasiliquid layer are not well known, but it is generally believed that the layer thickness is strongly temperature dependent, diverging to infinite thickness as the melting point is approached, and that the quasiliquid properties become similar to those of bulk water as the layer thickness increases. If true, then we would expect that the solid/quasiliquid interface should resemble the solid/liquid interface as the melting point is approached.

It is significant, therefore, that the measurements of  $\sigma_0$  and  $\Delta T_0$  cited above yield essentially the same molecular step energy, suggesting that the dynamical growth behaviors in both these cases arise from essentially the same physical phenomenon. To our knowledge, this correspondence between ice growth from water vapor and from liquid water has not yet been examined in the scientific literature. The data indicate that the solid/liquid and solid/quasiliquid interfaces yield comparable step energies over a substantial temperature range, a somewhat predictable statement that nevertheless was apparently not anticipated in previous investigations of surface premelting or ice crystal growth.

Below we examine these points in detail, using basic thermodynamics to connect ice growth from water vapor and ice growth from liquid water. We further suggest that many-body molecular-dynamics simulations of the *equilibrium* structure and energetics of the ice surface, including step energies and premelting, could be used to better understand the *non-equilibrium* dynamics of ice crystal growth over a broad range of conditions.

## 2 Nucleation Theory

For a simple monomolecular solid surface in contact with its pure melt or pure vapor, crystal growth is driven by a chemical potential jump at the interface – by a nonzero supercooling at the solid/liquid interface or by a nonzero supersaturation in the case of growth from vapor. For both these cases, a classical polynuclear growth model gives the normal growth velocity [6]

$$v_n \approx A_0 \Delta\mu \exp\left(\frac{-S\beta^2 a^2}{\Delta\mu kT}\right) \quad (1)$$

where  $S \approx 1$  is a geometrical factor,  $\beta$  is the step free energy (per unit length) at the crystal interface,  $a$  is the molecular size,  $\Delta\mu$  is the chemical potential jump at the interface,  $k$  is the Boltzmann factor and  $T$  is temperature. The prefactor  $A_0$  is somewhat model dependent, as the many-body microphysics at the interface is complex and not well understood, but it is expected that  $A_0$  has at most a weak dependence on  $\Delta\mu$ . We chose the functional form above so that  $v_n \sim \Delta\mu$  (the Wilson-Frenkel law [6]) when  $\Delta\mu$  is large enough that the exponential term goes to unity, as this is a generally accepted description of crystal growth in the absence of a nucleation barrier.

For ice growth from water vapor, we have  $\Delta\mu \approx \sigma kT$  for  $\sigma \ll 1$ , where  $\sigma = (c_{surf} - c_{sat})/c_{sat}$  is the supersaturation with respect to ice just above the growing surface,  $c_{surf}$  is the water vapor number density at the surface, and  $c_{sat}(T)$  is the equilibrium number density above a flat ice surface [6]. For nucleation-limited growth we write

$$v_n \approx A_{vap} \sigma e^{-\sigma_0/\sigma} \quad (2)$$

$$\sigma_0 = \frac{S\beta_{vap}^2 a^2}{k^2 T_m^2}$$

where  $\beta_{vap}$  is the step energy at the solid/vapor interface. The prefactor can be obtained from ideal-gas statistical mechanics when there is no kinetic barrier (Hertz-Knudsen growth [6]), giving

$$A_{vap} = v_{kin} = \frac{c_{sat}}{c_{solid}} \sqrt{\frac{kT}{2\pi m}} \quad (3)$$

where  $c_{solid} = \rho_{ice}/m$  is the number density for ice. Note that the growth rate is often written as  $v_n = \alpha v_{kin} \sigma$ , where  $\alpha \leq 1$  is known as the attachment coefficient [7].

For growth from liquid,  $\Delta\mu \approx \ell t$  for  $t \ll 1$ , where  $t = (T_m - T)/T_m$  is the dimensionless supercooling and  $\ell$  is the solid/liquid latent heat per molecule ( $\ell = 1.0 \times 10^{-20}$  J for ice), giving

$$\begin{aligned} v_n &\approx A_{liq} t e^{-t_0/t} \\ t_0 &= \frac{S\beta_{liq}^2 a^2}{\ell k T_m} \end{aligned} \quad (4)$$

The prefactor is determined by how fast liquid molecules diffuse into position to join the solid lattice, which can be estimated [6]

$$A_{liq} \approx \frac{\ell}{6\pi a^2 \eta_{eff}} \quad (5)$$

where  $\eta_{eff}$  is the effective viscosity for liquid near the surface. The kinetics of liquid water near an ice surface is nontrivial, and it is possible that  $\eta_{eff}$  may differ from the normal bulk viscosity near the melting point,  $\eta_0 \approx 1.8 \times 10^{-3}$  Pa-s. Nevertheless, assuming  $\eta_{eff} \approx \eta_0$  and using  $a \approx 0.32$  nm gives  $A_{liq} \approx 3$  m/sec. An alternative model based on the density functional theory of freezing yields  $A_{liq} \approx (kT_m/m)^{1/2} \approx 350$  m/sec [8].

In the case of ice growth from water vapor in the presence of surface premelting, we assume that any nucleation barrier must exist at the solid/QLL interface, and at some point the quasiliquid layer would be thick enough that  $\beta_{vap} \approx \beta_{liq}$ . In this case we obtain

$$\begin{aligned} \sigma_0 &\approx \frac{\ell}{k T_m} t_0 \\ &\approx 2.6 t_0 \end{aligned} \quad (6)$$

or equivalently  $\sigma_0 \approx 0.01 \Delta T_0$ , where  $\Delta T_0 = t_0 T_m$  is expressed in degrees C.

## 3 Experimental Data

### 3.1 Growth from Water Vapor

The experimental data from [1] are the most recent, most extensive, and we believe the most accurate measurements to date of the intrinsic ice growth rates of faceted basal and prism surfaces from water vapor. In particular, the experiments were performed at low pressures to reduce the effects of particle diffusion through the surrounding gas, and special attention was paid to determining  $\sigma_{surf}$ , the supersaturation at the growing surface. Over the temperature range  $-2 \text{ C} \geq T \geq -40 \text{ C}$ , the data are well described

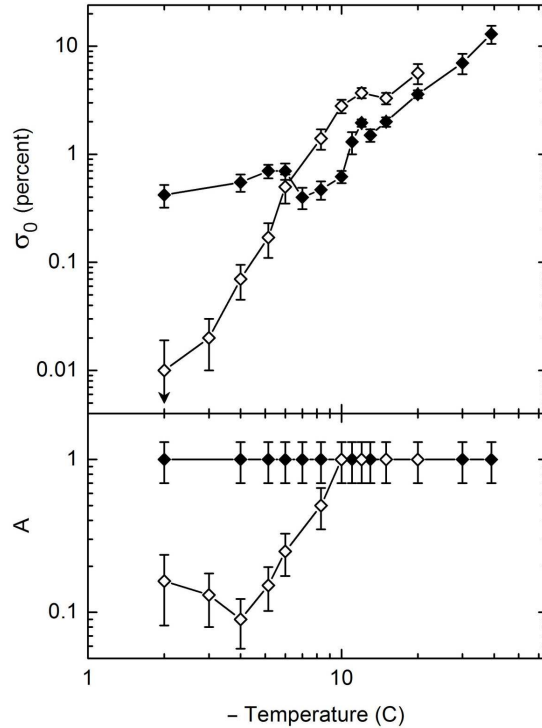


Figure 1: Measurements of the intrinsic growth rates of the principal ice crystal facets from water vapor. The growth velocity normal to the surface is described by  $v = \alpha v_{kin} \sigma_{surf}$ , where  $\sigma_{surf}$  is the supersaturation at the surface and the attachment coefficient is parameterized with  $\alpha(T, \sigma_{surf}) = A \exp(-\sigma_0/\sigma_{surf})$ . The solid points show the measured  $A(T)$  and  $\sigma_0(T)$  for the basal facets, while the open points describe measurements of the prism facets, from [1].

by a dislocation-free nucleation-limited crystal growth model, parameterized using  $v_n = \alpha v_{kin} \sigma_{surf}$  with  $\alpha(\sigma_{surf}, T) = A \exp(-\sigma_0/\sigma_{surf})$ . The measured parameters  $A(T)$  and  $\sigma_0(T)$  for the basal and prism facets are shown in Figure 1.

Our understanding of these data is quite crude, in part because our overall understanding of the many subtleties of crystal growth dynamics is somewhat rudimentary, especially in a material like ice that exhibits substantial surface premelting. In [9] we attempted to construct a comprehensive physical picture of ice growth from water vapor, connecting the growth measurements shown in Figure 1 with related morphological observations. Since our present purpose is to examine the correspondence between growth from water vapor and from liquid water, we will focus on the growth from vapor at  $T = -2$  C, which is the highest temperature for which we have data in Figure 1.

We focus especially on the basal facet growth at  $T = -2$  C, and these data are shown in more detail in Figure 2. As was described in [1], the prefactor  $A$  at this temperature was in part extrapolated from lower temperatures, since the basal data were consistent with  $A = 1$  over the entire temperature range of the measurements. This assumption of  $A = 1$  gave the fit parameters  $(A, \sigma_0) = (1, 0.0042)$  shown in Figure 1. As

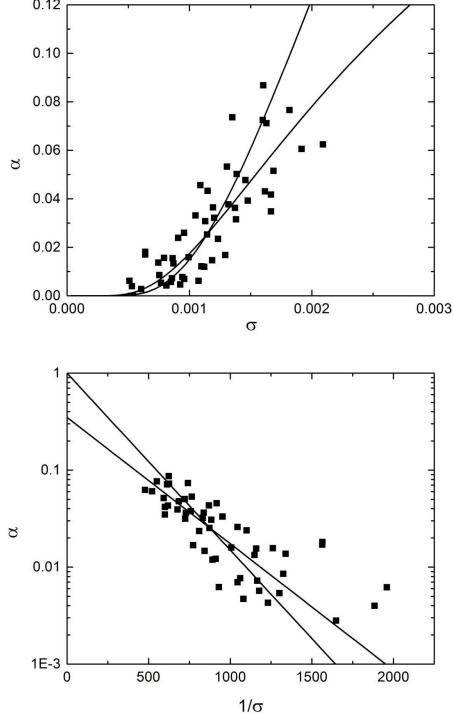


Figure 2: Measurements of the condensation coefficient  $\alpha$  for ice growth from water vapor, for the basal facet at -2 C as a function of near-surface supersaturation  $\sigma$ . The same data points are displayed two ways in the above plots. Both plots use the parameterizations  $v_n = \alpha v_{kin} \sigma$  and  $\alpha = A \exp(-\sigma_0/\sigma)$ , from [1]. The two fit lines show  $\alpha = \exp(-0.0042/\sigma)$  and  $\alpha = 0.35 \exp(-0.003/\sigma)$ . The lowest- $\sigma$  points were given a lower weight in the fits, as the growth was slowest for these points and we believed most susceptible to systematic errors. The two fit lines both describe the data reasonably well, roughly indicating the degree of uncertainty in extracting the parameters  $A$  and  $\sigma_0$  from the ice growth data.

is shown in Figure 2, however, the data at  $T = -2$  C are also reasonably well fit using  $(A, \sigma_0) = (0.35, 0.003)$ , and this figure demonstrates the uncertainty in extracting these parameters from the growth measurements. The data clearly indicate a nucleation-limited growth behavior, and from the fits we obtain  $\sigma_0 = 0.42 \pm 0.15$  percent, the uncertainty including our best estimate of possible systematic effects. The experiment and data analysis are described in more detail in [1].

### 3.2 Growth from Liquid Water

Although numerous observations of ice growth from liquid water have been reported in the literature, in most cases the growth rates are strongly limited by the diffusion of latent heat generated at the growing crystal surface, and in this case the bath supercooling  $\Delta T_\infty$  can be markedly different from  $\Delta T_{surf}$  at the interface. Since the interfacial temperature is the essential variable governing the growth dynamics, we restrict our attention to experiments where heat-diffusion effects have been carefully considered and modeled

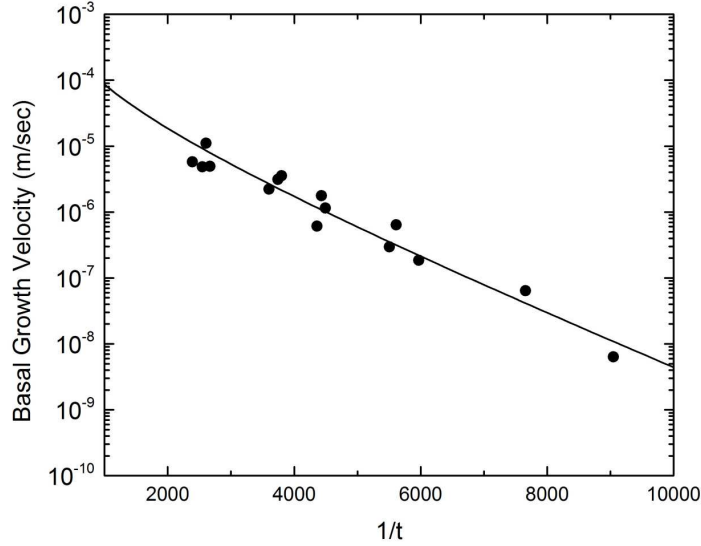


Figure 3: Measurements of the basal growth velocity as a function of  $t^{-1}$ , where  $t$  is the dimensionless supercooling, for ice growth from liquid water. The data are reproduced from [4], and the fit line is  $v_n = 0.2t \exp(-0.00084/t)$ , giving  $\Delta T_0 = tT_m = 0.24$  C.

to determine  $v_n(\Delta T_{surf})$ .

The work presented in [4] is the best we have found describing measurements of the basal growth rate as a function of supercooling, and the relevant data from this source are reproduced in Figure 3. In this series of measurements, the ice growth was observed in a thin capillary tube, allowing  $\Delta T_{surf}$  to be determined with good accuracy, and repeated zone refining was used to remove impurities from the water sample (it was found that impurities reduced the measured growth rates).

From the liquid growth data shown in Figure 3, together with the assumed functional form given in Equation 4, we extract the value  $\sigma_0 = \ell t_0 / kT_m = 0.24 \pm 0.04$  percent. Comparing with  $\sigma_0 = 0.42 \pm 0.15$  percent from the vapor growth data, we see that the two values are consistent with being the same to within the estimated uncertainties. This supports our hypothesis that ice growth from water vapor and ice growth from liquid water are related near the melting point, when significant surface premelting is present. In particular, these data show that the step free energy at the solid/QLL interface at  $T = -2$  C is quite close to the step energy at the solid/liquid interface near  $T = 0$  C. Extrapolating the basal  $\sigma_0$  data in Figure 1 to higher temperatures, we expect  $\sigma_0$  to approach  $\sigma_0 \approx 0.24 \pm 0.04$  percent as the temperature approaches the melting point.

The fit value  $A_{liq} \approx 0.2$  m/sec from Figure 3 is low compared to our estimate above using the viscosity of bulk liquid water, but this may be unique to the basal surface. Similar measurements described in [10] found growth rates as high as  $v_n = 0.077$  m/sec at a supercooling of  $\Delta T = 10$  C for nonbasal surfaces having a much lower nucleation barrier. Since thermal diffusion and any residual nucleation barrier both reduce the growth rate, this  $v_n$  measurement suggests a lower limit of  $A_{liq} > 2$  m/sec for nonbasal surfaces. Additional measurements in [11] describe ice dendrite tip velocities as high as 0.6 m/sec at  $\Delta T_\infty = 30$  C, again giving a lower limit of  $A_{liq} > 5$  m/sec for nonbasal surfaces at high growth rates.

On the prism surface, both ice growth from liquid water and ice growth from water vapor show much smaller nucleation barriers. The measured  $\sigma_0$  at  $-2$  C (see Figure 1) and  $t_0$  near the melting point [10] are both essentially indistinguishable from zero. The story is not as compelling as for the basal case, but nevertheless the data are consistent with the correspondence we are proposing. Both the basal and prism data suggest a smooth transition from solid/liquid growth to solid/vapor growth near the melting point. At lower temperatures the QLL becomes thinner and eventually disappears entirely, resulting in the complex growth behavior described in more detail in [9].

## 4 Discussion

The data described above suggest a rather simple picture of ice crystal growth from water vapor in the presence of surface premelting. At low supersaturations on the basal surface, the growth rate is strongly limited by the nucleation of molecular terraces at the solid/quasiliquid interface. Near the melting point, the step energy at this interface is approximately equal to the step energy at the solid/liquid interface. Thus there is a simple correspondence between ice growth from water vapor and ice growth from liquid water.

On the prism surface, or on the basal surface at high supersaturations, the growth is not strongly limited by a nucleation barrier. In this case the growth kinetics at the solid/quasiliquid interface are much faster than at the quasiliquid/vapor interface, as indicated by the fact that  $A_{liq} \gg A_{vap}$ , or equivalently  $A_{liq} \gg v_{kin}$ , by a large factor. In this situation the growth is limited by kinetics at the quasiliquid/vapor interface.

Assuming an essentially liquid surface, we therefore would expect  $A \approx 1$  for ice growth from water vapor [12]. The data in Figure 1 are consistent with this except on the prism facet at high temperatures. We have no explanation for this discrepancy. The physical picture described above is quite compelling, however, enough so that it suggests that there may be some currently unrecognized systematic error in the measurements. Additional data or analysis will likely be necessary to resolve this issue.

The data also suggest rather clearly that the key to understanding ice crystal growth is understanding the step energies on the different surfaces as a function of temperature. To my knowledge, relatively little attention has been given to using many-body molecular dynamics simulations to examine molecular step energies, although simulations of premelting and ice growth have been studied by a number of researchers [13, 14, 15, 16, 17, 18].

The fact that the step energy is an equilibrium quantity means that its calculation from molecular dynamics simulations could be substantially simpler than simulating full growth dynamics, as only equilibrium energetics calculations are needed. However, the measured step energies are quite low compared to expectations for a sharp molecular step ( $\beta \ll \beta_0$  in [1]). A simple geometrical argument then suggests that surface relaxation “smooths out” the terrace edge over perpendicular distances of perhaps  $20a$  near the melting point to minimize the overall surface energy in the vicinity of the step. If true, then simulations must include large surfaces to fully model the step energy. This smoothing is substantially less at lower temperatures, however, making the calculations relatively easier.

Regardless of the details, it appears there exists a substantial opportunity to use current many-body molecular dynamics simulations, with perhaps only minor modifications, to calculate step energies at the ice surface. If successful, these calculations could go far toward furthering our understanding of the dynamics of ice crystal growth.

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